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(54) Title: PROCESS FOR UNIMODAL STYRENIC FOAM STRUCTURE (57) Abstract Disclosed is a foamable styrenic polymer gel containing an aqueous blowing agent capable of forming a closed-cell, unimodal foam structure. The gel composes in admixture the flowable melt of a polymer composition having greater than 50 percent by weight of a styrenic polymer and a blowing agent having 1 percent or more by weight water based upon the total weight of the blowing agent. The styrenic polymer has a degree of water solubility sufficient to ensure formation of a unimodal foam structure instead of a bimodal foam structure. The unimodal cell size distribution provides desirable fabricability and machinability characteristics for the foam structure.		

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"PROCESS FOR UNIMODAL STYRENIC FOAM STRUCTURE"

The invention relates to a foamable styrenic polymer gel expandable to form a closed-cell, unimodal
5 foam structure with an aqueous blowing agent and a process for making the structure.

Due to present environmental concerns over the use of potentially ozone-depleting or flammable blowing
10 agents, it is desirable to make styrenic polymer foam structures with aqueous blowing agents. Such foam structures made with aqueous blowing agents can be seen in U.S. Patent No. 4,455,272, U.S. Patent No. 4,559,367, and European Patent Application 89114160.8.
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A problem with styrenic polymer foam structures made with aqueous blowing agents is the formation of bimodal cell structures of relatively larger primary
20 foam cells and relatively smaller secondary foam cells. The bimodal cell structure makes machining and fabricating difficult since the smaller secondary cells govern mechanical properties. Easy machinability and fabricability of foam structures is important in
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decorative, floral, novelty, and craft applications as well as tongue and groove cutting.

It would be desirable to have a closed-cell, styrenic polymer foam structure blown with an aqueous blowing agent that is easy to machine and fabricate. It would be desirable to have such a foam structure with a unimodal or primary cell size distribution.

According to the present invention, there is a foamable styrenic polymer gel capable of forming a closed-cell, unimodal foam with enhanced machinability and fabricability. The gel comprises in admixture a flowable melt of a styrenic polymer material having greater than 50 percent by weight of styrenic monomeric units and a blowing agent having at least 1 percent by weight water based upon the total weight of the blowing agent. The styrenic polymer melt has a water solubility sufficient to provide for formation of a styrenic polymer foam structure having a unimodal cell size distribution upon expansion of the gel. The desired level of solubility may be obtained by employing a styrenic polymer material of sufficiently low molecular weight or solubilizing or compatibilizing additives or polymers.

Further according to the present invention, there is a foamable styrenic polymer material as described above except that the blowing agent comprises a quantity of water sufficient to provide for formation of a foam structure having a substantially bimodal cell size distribution and consisting essentially of polystyrene of 200,000 weight average molecular weight with 20 weight percent or less of the polystyrene being

individual polymer molecules each less than 20,000 molecular weight.

Further according to the present invention, there is a process for making a closed-cell styrenic polymer foam structure having a unimodal cell size distribution. The process comprises: a) heating a styrenic polymer material having greater than 50 percent by weight styrenic monomeric units based upon the total weight of the styrenic polymer material to form a melt polymer material having a water solubility sufficient to provide for formation of a styrenic polymer foam structure having a substantially unimodal cell size distribution; b) incorporating into the melt polymer material at an elevated temperature a blowing agent comprising 1 percent or more by weight water based upon the total weight of the blowing agent to form a foamable gel; and c) expanding the foamable gel through a die to form a foam structure.

The styrenic polymer foamable gel of the present invention forms, upon expansion, a foam structure having a unimodal cell size distribution. Forming a unimodal foam structure from a foamable gel containing certain quantities of an aqueous blowing agent is heretofore unknown because aqueous blowing systems typically cause formation of foam structures with a bimodal cell size distribution.

Unimodal foam structures and bimodal foam structures differ in the configuration of their respective cell size distributions. A unimodal cell size distribution is one in which the cells are of a generally uniform size throughout the foam structures, except for the skin regions in the case of extruded

foam. A bimodal cell size distribution is one in which there is one group of relatively larger primary foam cells of generally uniform size and another group of relatively smaller secondary foam cells of generally uniform size ranging in average cell size from 5 percent to 50 percent of the average cell size of the primary cells. The secondary cells may be situated within the cell walls or struts of the primary cells, or may be situated outside of or adjacent to the primary cells individually or in groups of two or more. A strut is a juncture of three or more cell walls. The primary cells may be generally dispersed throughout the secondary cells such that the foam structure has a generally heterogeneous dispersion of the two cell types throughout. Additional teachings directed to foam structures with bimodal cell distributions are seen in United States Patent Nos. 4,455,272 and 4,559,367, U.S. Serial Nos. 07/895,970 filed June 9, 1992 and 07/896,025 filed June 9, 1992, and European Patent Application No. 89114160.8.

The prior art is instructive concerning processes for making bimodal foam structures with aqueous blowing agent systems. U.S. Patent No. 4,559,367 relates a process for making a bimodal foam structure by incorporating finely-divided, water-containing organic vegetable matter into a polymer feedstock, melting the resulting solid mixture, incorporating a volatile foaming agent into the solid mixture melt to form a foamable mixture, and extruding the foamable mixture through a die to form the foam structure. U.S. Patent No. 4,455,272 relates a process for making a bimodal foam structure by injecting water and a physical blowing agent into a polymer melt and

extruding the resulting mixture through a die to form the structure. EPO Application No. 89114160.8 relates a process for making a bimodal foam structure by incorporating into the polymer feedstock a fine, water-absorbing mineral powder, melting the resulting solid mixture, incorporating a volatile foaming agent into the solid mixture melt to form a foamable mixture, and extruding the foamable mixture through a die to form the foam structure.

Though not bound by any particular theory, bimodal cell size distributions are believed to result when foamable gels contain a level of water exceeding the solubility of water in the polymer melt at the extant processing conditions (for example, temperature, pressure, mechanical agitation, etc.). The excess water manifests itself in the form of secondary cells upon expansion of the foamable gel to a foam structure.

Use of aqueous blowing agent systems comprising 1 or more weight percent or more water by weight based upon the total weight of the blowing agent typically result in bimodal foam distributions in foam structures made from commercially-available styrenic polymers, particularly polystyrene.

The present invention sets forth a process for making a closed-cell, unimodal foam structure with an aqueous blowing agent system and a foamable gel expandable to form such structure. An important feature of the invention is the formation of a foamable gel having a level of water solubility sufficiently high to enable expansion of the gel to form a unimodal foam structure and avoid formation of a bimodal foam structure. A sufficiently high level of water

solubility may be attained by selecting a styrenic polymer material of requisite water solubility or by addition of solubilizing or compatibilizing agents to the styrenic polymer material. Desirably, the polymer material will have a water solubility of 0.4 parts or
5 more water and more desirably 3 parts or more water by weight per hundred parts by weight polymer melt at 125°C. The 0.4 parts level is approximately the lower limit of solubility in which a conventional polystyrene
10 resin will form the desired unimodal foam structure.

The present foam structure comprises a styrenic polymer material. Suitable styrenic polymer materials include styrenic homopolymers and copolymers of styrenic
15 compounds and copolymerizable ethylenically unsaturated comonomers. The styrenic polymer material may further include minor proportions of non-styrenic polymers. The styrenic polymer material may be comprised solely of one or more styrenic homopolymers, one or more styrenic
20 copolymers, a blend of one or more of each of styrenic homopolymers and copolymers, or blends of any of the foregoing with a non-styrenic polymer. Regardless of composition, the styrenic polymer material comprises greater than 50 and preferably greater than 70 weight
25 percent of styrenic monomeric units. Most preferably, the styrenic polymer material is comprised entirely of styrenic monomeric units. The styrenic polymer material preferably has a weight average molecular weight of
30 100,000-350,000 according to size exclusion chromatography.

Suitable styrenic polymers include those derived from styrenic compounds such as styrene, alphas-methylstyrene, ethylstyrene, vinyl benzene, vinyl toluene, chlorostyrene, and bromostyrene. Minor amounts

of monoethylenically unsaturated compounds such as C₁₋₄ alkyl acids and esters, ionomeric derivatives, and C₂₋₆ dienes may be copolymerized with styrenic compounds. Examples of copolymerizable compounds include acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, acrylonitrile, maleic anhydride, methyl acrylate, ethyl acrylate, butyl acrylate, propyl acrylate, methyl methacrylate, vinyl acetate, vinyl alcohol, amides, 1,3-butadiene, 1,3-pentadiene, and 1,4-hexadiene. Preferred structures comprise substantially polystyrene (that is, greater than 80 percent by weight) and most preferably entirely of polystyrene because polystyrene foam is economical, and is commonly employed as an insulating plastic foam.

A means of attaining a sufficient level of water solubility in the styrenic polymer melt of the foamable gel is to incorporate previously-processed or recycled styrenic polymer into the melt. The lower molecular polymers, oligomers, and inorganic foam processing additives increase the water solubility of the melt over a corresponding melt without the previously-processed or recycled styrenic polymer. The lower molecular weight polymers and oligomers are present in the previously-processed or recycled styrenic polymer because of the process shearing and temperature degradation the previously-processed or recycled styrenic polymer previously underwent.

Another means of attaining a sufficient level of water solubility is to incorporate into the styrenic polymer material melt minor proportions (that is, less than 15 weight percent) of relatively hydrophilic polymers or copolymers such as polyethylene, polyvinyl acetate, polyacrylonitrile, and C₁₋₄ polycarboxylic

acids and acrylates. The relatively hydrophilic polymers increase the water solubility of the styrenic polymer material melt over a corresponding polymer melt without the hydrophilic polymers.

5 Another means of attaining a sufficient level of water solubility is to incorporate a solubilizing or compatibilizing agent into the styrenic polymer material melt to increase the water solubility of the melt over a
10 corresponding polymer melt without the agent. The agent would increase water solubility of the melt in the typical foaming temperature range for styrenic polymers of between 110°C-135°C. The agents are at least partly soluble in both the melt and water. Representative
15 solubilizing or compatibilizing agents include the following:

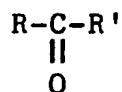
saturated and unsaturated aliphatic or aromatic alcohols having the formula

20



wherein R is a linear or cyclic alkyl or alkenyl group having 1-10 carbon atoms;

25 ketones having the formula



30 wherein R and R' are aliphatic or aromatic groups of 1-10 carbon atoms;

carboxylic acids having the formula



5 wherein R is an H (hydrogen atom) or an aliphatic or aromatic group of 1-10 carbon atoms;

esters having the formula



10 wherein R and R' are an H or aliphatic or aromatic groups of 1-10 carbon atoms;

aldehydes having the formula



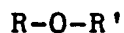
wherein R is an aliphatic or aromatic group of 1-10 carbon atoms;

20 aliphatic and aromatic amines having the formula



25 wherein R is an aliphatic or aromatic group of 1-10 carbon atoms; and

ethers having the formula



30 wherein R and R' are aliphatic or aromatic groups of 1-10 carbon atoms.

The unimodal structure may contain additional additives such as pigments, fillers, antioxidants,

extrusion aids, nucleating agents, stabilizing agents, antistatic agents, fire retardants, or acid scavengers.

The foam component of the unimodal foam structure preferably has density of 16 to 80 kilograms per cubic meter. The foam component further preferably has an average cell size of 0.05 to 2.4 millimeters.

The unimodal foam structure is generally formed by melting and mixing the styrenic polymer itself or with other polymers if present to form a plastic melt, incorporating a blowing agent into the plastic melt to form a foamable gel, and extruding the foamable gel through a die to form the foamed structure. During melting and mixing, the polymers are heated to a temperature at or above the glass transition temperature or at or above the melting point of the polymer. Melting and mixing of polymers and any additives is accomplished by any means known in the art such as with an extruder, mixer, or blender. Likewise, the blowing agent, including water, is incorporated or blended into the plastic melt by any of the same above-described means. The blowing agent is blended with the plastic melt at an elevated pressure sufficient to prevent substantial expansion of the resulting plastic gel or loss of generally homogeneous dispersion of the blowing agent within the gel. The blowing agent is incorporated into the melt in a weight proportion of between 1 to 30 parts and preferably from 3 to 15 parts per hundred parts of the polymer to be expanded. The foam gel is preferably passed through a cooler or cooling zone to lower the gel temperature to an optimum foaming temperature. For polystyrene, typical optimum foaming temperatures range from 110°C to 135°C. The cooled gel is then passed through the die into a zone of lower or

reduced pressure to form the foam structure. The zone of lower pressure is at a pressure lower than that in which the foamable gel is maintained prior to extrusion through the die. The lower pressure may be superatmospheric or subatmospheric (vacuum), but is preferably at an atmospheric level.

Water preferably comprises 1 weight percent or more and more preferably 3 weight percent or more of the blowing agent based upon the total weight of the blowing agent. Water may be incorporated into the polymer melt or polymer feedstock in the form of a water-carrying or water-generating solid, a liquid, or a vapor or gas. Incorporation of water in the form of a liquid or vapor is preferred.

The level of water in the blowing agent sufficient to provide the unimodal foam structure may alternately be characterized relative to the level necessary to provide a bimodal foam structure comprised of polystyrene commonly employed commercially to make foam structures. A commonly-employed polystyrene consists essentially of polystyrene of 200,000 weight average molecular weight with 20 weight percent or less of the polystyrene being of individual polymer molecules each less than 20,000 molecular weight as determined by size exclusion chromatography. The molecular weight of 20,000 corresponds approximately to the lower threshold of entanglement molecular weight for the polystyrene. A maximum fraction of low molecular weight molecules is specified to better characterize the polystyrene since the low molecular weight fractions of the polystyrene substantially determine its extent of water solubility. The commonly-employed polystyrene is described as consisting essentially of polystyrene since it refers to

a certain reference polystyrene irrespective of other polymers or agents which may impact the water solubility of the reference (commonly-employed) polystyrene. The foamable gel of the present invention may comprise a level of water sufficient in a foamable gel of the
5 reference (commonly-employed) polystyrene to form a bimodal foam structure of the reference polystyrene. The present foam gel nonetheless comprises a styrenic polymer material having a water solubility sufficient to
10 result in a foam structure of a substantially unimodal cell size distribution.

The styrenic polymer material of the present foamable gel is not limited in any way to the reference
15 (commonly-employed) polystyrene referred to above. As stated previously, the styrenic polymer material may vary in weight average molecular weight from 100,000 to 350,000. The reference to the commonly-employed resin is made so that the water content of the blowing agent
20 and the water solubility of the melt material may be described functionally without referring to specific quantities or proportions of water.

Blowing agents which may be utilized in
25 combination with water include inorganic agents, organic blowing agents and chemical blowing agents. Suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, air, nitrogen, and helium. Organic
30 blowing agents include aliphatic hydrocarbons having 1-9 carbon atoms and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, and neopentane. Fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and

chlorofluorocarbons. Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane, 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoro-ethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Chemical blowing agents include azodicarbonamide, azodiisobutyro-nitrile, benzenesulfonhydrazide, 4,4-oxybenzene sulfonyl-semicarbazide, p-toluene sulfonyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine.

Preferred blowing agents are those using a combination of water and an inorganic blowing agent such as nitrogen, carbon dioxide, krypton, or argon. A useful blowing agent comprises water and carbon dioxide. The blowing agent preferably comprises from 1 to 80 weight percent water, more preferably from 3 to 80

weight percent water, and most preferably between 5 and 60 weight percent water based upon the total weight of the blowing agent.

5 The unimodal foam structure is preferably closed-cell, and has a closed-cell content of at least 90 percent according to ASTM D2856-87.

10 Though the preferred process for making the present structure is an extrusion process, it is understood that the above structure may be formed by expansion of beads, which may be molded at the time of expansion to form structures of various shapes. Insulating panels formed from molded, expandable beads are commonly referred to as bead board.

15 The unimodal foam structure may be used to insulate various surfaces by applying to the surface an insulating panel fashioned from the present structure. Such panels may be used in any conventional insulating application such as roofing, buildings, refrigerators, etc.

20 The unimodal foam structure may also be formed into a variety of plurality of discrete foamed particles for conventional loose-fill cushioning and packaging applications.

25 The following are examples to illustrate various aspects of the present invention, and are not to be construed as limiting. All percentages and parts are by weight unless otherwise noted.

Example 1

Foam structures were made with an apparatus comprising a single-screw extruder, mixers, a cooler, and a die in series. A blend of 70 percent by weight general Purpose Polystyrene (200,000 weight average molecular weight by size exclusion chromatography) (The Dow Chemical Company) and 30 percent by weight recycle polystyrene of 150,000 weight average molecular weight according to size exclusion chromatography was fed to the extruder. 0.05 parts per hundred magnesium oxide, 0.05 parts per hundred calcium stearate, and 1.0 parts per hundred hexabromocyclododecane by weight were added to the polystyrene in the extruder. 1.5 parts per hundred water and 4 parts per hundred carbon dioxide mixture were added to the polymer melt in the mixer to form a foamable gel. The foamable gel was cooled to 125°C and extruded through the die and expanded between substantially parallel forming plates. The die pressure was 1100 pounds per square inch (psig). The foam structure had a unimodal cell size distribution with a relatively large average cell size of 0.2 millimeter (mm) and a density of 2.1 pounds per cubic foot (pcf). The machinability of the foam structure was excellent as determined by the router test.

Example 2

Styrenic polymer foam structures were made using the same formulation and the apparatus of Example 1 except that the blowing agent comprised 2.0 pph water and 2.0 pph carbon dioxide. The foam had a unimodal cell size distribution of 1.7 mm and a density of 2.0 pcf. The machinability of these foam structures was good as determined by the router test.

CLAIMS

1. A process for making a styrenic polymer foam structure with a unimodal cell size distribution, comprising:

- 5 a) heating a styrenic polymer material having greater than 50 percent by weight styrenic monomeric units based upon the total weight of the styrenic polymer material to form a melt polymer material;
- 10 b) incorporating into the melt polymer material at an elevated pressure a blowing agent comprising 1 weight percent or more water based upon the total weight of the blowing agent to form a foamable gel; and
- 15 c) expanding the foamable gel at a reduced pressure to form a foam structure; the process being characterized in that the styrenic polymer material has a water solubility sufficient to provide for formation of a styrenic polymer foam structure of a unimodal cell size distribution upon expansion of the foamable gel.

20 2. The process of Claim 1, wherein the foamable gel is cooled to an optimum foaming temperature and extruded through a die to a zone of reduced pressure to form the foam structure.

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3. The process of Claims 1 or 2, wherein a nucleating agent is incorporated into the melt polymer material.

4. The process of Claims 1, 2, or 3, wherein the blowing agent incorporated into the melt polymer material is 3 percent or more by weight water based upon the total weight of the blowing agent.

5. The process of Claim 1, 2, or 3, wherein the polymer melt material has a water solubility of 0.4 parts or more by weight water per hundred parts by weight melt polymer material at 125°C.

6. The process of Claim 1, 2, or 3, wherein a solubilizing agent is incorporated into the melt polymer material to increase the water solubility relative to a corresponding melt polymer material without the solubilizing agent.

7. The process of Claims 1, 2, or 3, wherein the polymer melt material has a water solubility of 3 parts or more by weight water per hundred parts by weight melt polymer material at 125°C.

8. A process for making a styrenic polymer gel foam structure with a unimodal cell size distribution, comprising:

a) heating a styrenic polymer material having greater than 50 percent by weight styrenic monomeric units based upon the total weight of the styrenic polymer material to form a melt polymer material;

b) incorporating into the melt polymer material a blowing agent to form a foamable gel wherein the blowing agent has a quantity of water sufficient to provide for formation of a foam structure having a

substantially bimodal cell size distribution and consisting essentially of polystyrene of 200,000 weight average molecular weight with 20 weight percent or less of the polystyrene being of individual polymer molecules each less than 20,000 molecular weight; and

5 c) expanding the foamable gel at a reduced pressure to form the foam structure; the process being characterized in that the styrenic polymer material melt has a water solubility sufficient to provide for formation of a styrenic polymer foam structure of a
10 unimodal cell size distribution upon expansion of the foamable gel.

9. A unimodal styrenic polymer foam structure obtainable by the process of any of the above claims.

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AMENDED CLAIMS

[received by the International Bureau on 23 February 1994 (23.02.94) ;
original claims 4-7 and 9 amended ; other claims
unchanged (2 pages)]

3. The process of Claims 1 or 2, wherein a nucleating agent is incorporated into the melt polymer material.

5 4. The process of Claim 1 or 2, wherein the blowing agent incorporated into the melt polymer material is 3 percent or more by weight water based upon the total weight of the blowing agent.

10 5. The process of Claim 1 or 2, wherein the polymer melt material has a water solubility of 0.4 parts or more by weight water per hundred parts by weight melt polymer material at 125°C.

15 6. The process of Claim 1 or 2, wherein a solubilizing agent is incorporated into the melt polymer material to increase the water solubility relative to a corresponding melt polymer material without the solubilizing agent.

20 7. The process of Claim 1 or 2, wherein the polymer melt material has a water solubility of 3 parts or more by weight water per hundred parts by weight melt polymer material at 125°C.

25 8. A process for making a styrenic polymer gel foam structure with a unimodal cell size distribution, comprising:

30 a) heating a styrenic polymer material having greater than 50 percent by weight styrenic monomeric units based upon the total weight of the styrenic polymer material to form a melt polymer material;

b) incorporating into the melt polymer material a blowing agent to form a foamable gel wherein the blowing agent has a quantity of water sufficient to provide for formation of a foam structure having a

AMENDED SHEET (ARTICLE 19)

substantially bimodal cell size distribution and consisting essentially of polystyrene of 200,000 weight average molecular weight with 20 weight percent or less of the polystyrene being of individual polymer molecules each less than 20,000 molecular weight; and

- 5 c) expanding the foamable gel at a reduced pressure to form the foam structure; the process being characterized in that the styrenic polymer material melt has a water solubility sufficient to provide for formation of a styrenic polymer foam structure of a
10 unimodal cell size distribution upon expansion of the foamable gel.

9. A unimodal styrenic polymer foam structure obtainable by the process of Claim 1, 2, or 8.

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AMENDED SHEET (ARTICLE 19)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/10144

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B29D 11/00

US CL :521/74, 79, 80, 82, 97, 142, 146, 910; 264/50, 51

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 521/74, 79, 80, 82, 97, 142, 146, 910; 264/50, 51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Styrene, Foam, Blowing Agent, Unimodal, Cell Size, Nucleating Agent, Solubilizing Agent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US, A, 5,244,927 (BINDER) 14 SEPTEMBER 1993, see entire document.	1-3, 8
A	US, A, 4,455,272 (SCHUBERT) 19 JUNE 1984, see entire document.	1-3, 8
A	US, A, 4,559,367 (HURPS) 17 DECEMBER 1985, see entire document.	1-3, 8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

16 DECEMBER 1993

Date of mailing of the international search report

FEB 14 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/10144

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-7, 9
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

PCT/EP 00/06297

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08J9/12 C08J9/00 //C08L25/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 197 09 119 A (BASF AG) 10 September 1998 (1998-09-10) page 3; examples claims	1
Y	WO 96 14354 A (SOLVAY FLUOR & DERIVATE ;KRUECKE WERNER (DE)) 17 May 1996 (1996-05-17) page 6, line 13 -page 7, line 20 page 20-21; example 3 claims	1
A	WO 99 16815 A (TENNECO PACKAGING INC) 8 April 1999 (1999-04-08) claims	1
-/-		
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. </div> <div> <input checked="" type="checkbox"/> Patent family members are listed in annex. </div> </div>		
* Special categories of cited documents :		
<div style="display: flex;"> <div style="width: 50%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">15 November 2000</div>	Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">22/11/2000</div>	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <div style="text-align: center; font-weight: bold;">Oudot, R</div>	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06297

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 340 844 A (WELSH GARY C ET AL) 23 August 1994 (1994-08-23) column 4, line 23-25 claims	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 00/06297

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9614354 A	17-05-1996	DE 4439082 A	09-05-1996
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